

CERTAIN PROCEDURES IN UTILIZING KANSAS
NATURAL GAS AS A CARBURIZING AGENT

by

FRANK JACOBS, JR.

B. S. Kansas State College of
Agriculture and Applied Science, 1950

A THESIS

submitted in partial fulfillment of the
requirements for the degree

MASTER OF SCIENCE

Department of Shop Practice

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1951

02-6-52 CF

Docu-
ments
LO
2668
T4
1951
J36
C.2

11

TABLE OF CONTENTS

INTRODUCTION	1
REVIEW OF LITERATURE	6
THE CARBURIZING PROCESS	11
CARBURIZING ATMOSPHERES	18
APPARATUS AND EQUIPMENT	31
EXPERIMENTAL PROCEDURE	43
METHODS OF ANALYSIS	45
Dew Point Determination	45
Gas Analysis	46
Case Depth Determination	46
DISCUSSION OF RESULTS	51
SUMMARY AND CONCLUSIONS	73
ACKNOWLEDGMENT	74
LITERATURE CITED	75

INTRODUCTION

Carburizing is a heat treating process applied to ferrous metals with the object of increasing the carbon content of the surface layer so that this layer will be substantially harder than the underlying metal after proper heat treatment. The case is high in carbon content which results in better wear resistance while the core is of low carbon content for toughness and shock or impact resistance. The process of carburizing and hardening has long been known as "case hardening."

The mechanism whereby the carbon from some outside source enters the iron or steel is quite complex. Following is a listing of the allotropic forms (30) of iron (1 to 4) which are stable within the temperature ranges indicated:

- (1) Alpha - - - - - Stable up to 1350° F.
- (2) Beta - - - - - 1350 to 1670° F.
- (3) Gamma - - - - - 1670 to 2550° F.
- (4) Delta - - - - - 2550 to 2800° F.
- (5) Liquid - - - - - 2800° F. and above

In the alpha form, iron can dissolve up to about 0.04 percent carbon. In the gamma form, iron can take into solution up to about 1.98 percent carbon. The delta and liquid forms are of no concern in carburizing because in carburizing, the steel is put into the gamma form.

The popular concept of carburizing is that carbon from an outside source such as a liquid, solid or gas, dissolves in the gamma iron at the surface and proceeds to diffuse inward at a rate dependent upon such factors as time, temperature and the carburizing medium.

The common carburizing temperature range is from 1600 to 1750° F. The solubility of the carbon in the steel increases with temperature above the transformation temperature range where alpha changes to gamma iron. Higher temperatures also permit higher rates of diffusion but too high a carburizing temperature may be undesirable because of such factors as: grain growth, distortion, and the effect on the carburizing furnace or retort. Carburizing is seldom done at temperatures in excess of 1750° F. in industrial practice.

At these temperatures, iron and carbon react to form the compound cementite (Fe_3C). At the carburizing temperature, the cementite is in solid solution with the gamma iron and is known as austenite. Because cementite is hard and brittle, it gives hardness and strength to steels particularly when the physical form of the cementite is regulated by heat treatment.

According to the iron carbon diagram in the Metals Handbook (27), up to about 1.98 percent carbon can be dissolved in the gamma iron. However, this is very seldom approached in commercial practice. The aim is generally to obtain from 0.85 to 1.20 percent carbon.

The absorption of carbon is only the first step in carburizing. Other phases are involved:

- (1) Diffusion of the carbon in the austenite.
- (2) Prevention of decarburization during diffusion or during cooling.
- (3) Selection of the proper heat treatment after carburizing to obtain desired physical properties.

Such factors as: the type of steel, carburizing medium, temperature, equipment and the case characteristics desired are to be considered.

The process of heat treating carburized steel involves quenching at a rate equal to or exceeding the critical cooling rate (27). Oil, molten salts, water, and brine are the common quenching mediums. During quenching, the cementite becomes dispersed throughout the transformed alpha iron (ferrite). It forms martensite which Sisco (30) defines as a super saturated solid solution of submicroscopic particles of cementite in the alpha iron lattice.

Carbon may be added to the steel surface by using a solid carbonaceous compound, a molten salt bath, or a gaseous carburizing media. When using a solid compound such as wood charcoal, coke, or bone, the pieces to be carburized are packed in the compound and heated to the carburizing temperature. An energizer such as barium carbonate is usually added to the compound. This produces carbon dioxide (CO_2) which reacts with hot carbon to

form carbon monoxide (CO). The carbon monoxide then reacts with the iron to form cementite. In gas carburizing, an atmosphere of pure carbon monoxide is relatively feeble as a carburizing agent. However, with solid compounds, the carbon source occludes the reaction product gases and there is an ample supply of carbon in an active form. In liquid salt carburizing baths, the carburizing action depends primarily on sodium cyanide, activated or catalyzed by such salts as barium, calcium or strontium. Liquid carburizing baths have some advantages over pack or gas carburizing in that they have a high heat conductivity, and due to their fluidity are uniform in temperature and are easy to control. In gas carburization, a wide range of hydrocarbons and their mixtures with carbon monoxide are employed. Only a small percentage of methane (CH_4) (balance hydrogen) is required in order to effect carburization.

There are a number of advantages in carburizing with gas. They include: lower cost of carburizing medium, continuous carburizing, automatic tempering operations in continuous furnaces and bright hardening, all of which help to lower the labor costs. Continuous carburizing furnaces allow production line set-ups for the heat treating operations.

The development of a controlled atmosphere for carburizing has been an outstanding accomplishment of recent years in the metallurgical field. Many types of atmospheres and generating equipment are now available. The idea of gas carburizing dates back to the middle of the 19th century but it was not until when

production requirements of World War II necessitated more suitable equipment that furnace manufacturers concentrated on this phase of design.

However, the cost of equipment for gas carburizing is still prohibitive for the small manufacturing plant or machine shop that does not have a large volume of work to be carburized. For this reason, the problem of utilizing Kansas natural gas as a carburizing agent in a small furnace of simple design, was undertaken.

This thesis problem has involved the design, construction, and utilization of a retort type of gas carburizing furnace. The design was approached with the objective of producing a gas carburizing unit that would be low in cost, easily controlled, and one that would work without an outside generator for the preparation of a "carrier" gas. A tube containing charcoal was included within the retort and was therefore at the carburizing temperature. Mixtures of gas and air were passed through this tube at various proportions and at selected temperatures. The chemical reaction resulting because of the air flowing through the charcoal was $C + 1/2O_2 + 2N_2 = CO + 2N_2$. The CO and CO₂ contents of the gas are determined by the reaction temperature, the CO increasing and the CO₂ decreasing with temperature increases.

The resulting atmosphere contains methane which has not dissociated and has a high hydrogen content. The heated charcoal reduces any highly oxidizing components such as CO₂ and converts

water vapor largely to hydrogen and carbon monoxide. These reactions, all taking place within this inner tube is the main feature of the carburizing apparatus.

REVIEW OF LITERATURE

The development of controlled atmospheres for heat treatment has been brought about by the many investigations of the reactions and equilibrium characteristics of the basic gases.

The underlying scientific idea of gas carburizing dates back to the middle of the 19th century but it was not until the 20th century that some attempt was made to control atmospheres. The major part of the development started early in 1913, soon after the results of Giolitti's (11) investigation became available. Giolitti summarized the literature up to 1912 in his "Cementation of Iron and Steel." He described experiments to determine the required conditions for successful gas carburizing and attempted to evaluate various gaseous atmospheres contributing much toward stimulating the development of the process on a practical basis. His book was translated from the Italian and published in the United States in 1915. Investigators later found some of his conclusions to be inadequately founded.

The first patent for a commercial, rotary type of furnace was applied for in 1905 by A. W. Machlet of the American Gas Furnace Company of New Jersey (37). The Buick Motor Company installed ten rotary furnaces in 1909 (37).

Experimental work was conducted initially on the stationary retort type of gas carburizing furnace. However, due to the heavy soot deposits which eventually plugged the inlets and outlets as well as forming a heavy layer on the charge which interfered with carburization, the experiments were abandoned.

By 1913, a spiral arrangement was worked out, whereby, the rotary furnace became a continuous gas carburizing furnace. The tumbling action of the rotary furnace kept the soot from depositing on the charge. By this time, it became apparent that gas carburizing could be developed on a commercial scale. The Timken Roller Bearing Company was one of the first to collect experimental data on gas carburizing.

The problem of gas carburization rapidly developed into a search for a gas tight retort that would withstand the carburizing temperature. The long time interval between the experimental verification of the possibilities of gas carburization and its commercial success was due principally to the lack of a suitable material for a retort. The growth of the automobile industry and the first World War brought about an increased commercial activity. The rotary furnace was still the main type of installation. By 1925, the retort problem was solved by the development of heat resisting alloys and it was at about this time that the first vertical stationary carburizing furnace was installed.

City gas was a common carburizing medium used but because it was unreliable in composition, a gas generator using charcoal

was supplied with the furnace as auxiliary equipment. Gases were bubbled through gasoline for the pickup of hydrocarbons.

Interest in gas carburizing was first centered on obtaining an atmosphere with a high carbon potential. Attention was not focused on the problem of sooting until "carrier" gases were produced. With the development of carrier gases came the horizontal, continuous, gas carburizer. A cheaper carburizing medium played a great part in this development.

Bramley and his associates (2) investigated effects of the rate of flow, temperature, and time using carbon monoxide alone and with the addition of other gases. He also investigated the diffusion characteristics of carbon in steel. His results showed that dry carbon monoxide was much more effective than carbon monoxide containing water vapor.

Sykes (33) explored the dissociation equilibrium conditions of methane at various temperatures. Sykes then saturated hydrogen with methane at various temperatures and investigated the effect of time and increasing methane concentration. His conclusions listed below are evident in contemporary commercial practice:

- (1) The temperature is the most important factor controlling the depth of case obtained when using a given carbon potential.

- (2) If the carbon potential of the gas is more than minimum at any given temperature, the rate of penetration is fixed by the rate of diffusion of the carbon in austenite. This is controlled by the carburizing temperature.

(3) At the higher carburizing temperatures, an increase in the concentration of methane results at first in greater case depth. If this concentration increases, it only raises the carbon concentration at the surface.

In 1930, Wilbur and Comstock (35) stated that any hydrocarbon gas, regardless of its available carbon content, could be used as a carburizing medium. They described an intermittent surge method and also summarized hydrocarbon reactions that are important in gas carburizing.

In 1933, Cowan (6) described successful carburizing experiments with natural gas, propane, butane, and acetylene in combination with flue gas. The carbon dioxide of the flue gas reacted with the carbon deposited on the parts to form carbon monoxide which effected carburization. This brought about the development of a continuous carburizing furnace with three distinct zones. The work in the zone near the entrance became coated with soot due to partial dissociation of the hydrocarbons. In the second zone, carburization took place. In the third zone, carburization was slowed down and time was allowed for diffusion, permitting a gradual carbon gradient.

Stansel (32) presented equilibrium data on various gases composing a carburizing atmosphere. Stansel's curves are based on equilibrium with austenite saturated with carbon at a given temperature.

In 1935, McQuaid (26) presented condensed summaries and requirements for successful gas carburizing.

In 1935, Gillett (9) discussed the equilibrium of controlled atmospheres for carburizing and the procedures for carburizing. He stated that carbon dioxide and hydrogen have a definite function beyond securing a less variable atmosphere, this function being the formation of an oxidized surface which has a catalytic action on the carburizing gas. It was observed at this time that metal muffles or retorts containing nickel and chromium caused much decomposition of the gas and changed the carburizing proportions.

Becker (1) evaluated the $\text{CO}_2:\text{CO}$ ratio for equilibrium of the gas mixture with steels of varying carbon content.

Guthrie and Wozasek (14) had stated that some moisture was necessary to get rapid carburization. There is much discussion on this point and not complete agreement among the authors. Due to the variable composition of city gas, he suggested using natural gas, propane or butane.

Practically all phases of carburizing were reviewed and discussed in the "Carburizing Symposium" (4) of the American Society for Metals in 1938.

In 1942, furnace atmospheres were reviewed and discussed in "Controlled Atmospheres" (5) by the American Society for Metals.

Holding a charge in a carburizing furnace indefinitely without ultimate change of the carbon content of the material has been in practice since 1946 (34). The gas used is essentially in equilibrium with the carbon content at the surface of the steel during the suspension period. This condition is maintained

until production is resumed at which time the temperature is brought up to the carburizing temperature and the regular carburizing atmosphere restored. The suspended carburization process eliminates the loss of production time due to week-ends and unforeseen production delays when carburizing furnaces of the continuous type are used.

The Holcroft Company (20) has eliminated the need for an outside generator for carrier gases. The carburizing furnace utilizes the "spent" gases from the carburizing chamber as the carrier gas. A small amount of original hydrocarbon gas is mixed with the exhaust gases and this mixture is then recirculated back through the carburizing chamber to serve as a carburizing atmosphere. A daily gas analysis is made for control purposes.

THE CARBURIZING PROCESS

In gas carburizing, the carbon of the atmosphere is in the form of gaseous hydrocarbons or carbon monoxide or both. When natural or manufactured gas is used methane and ethane are the principle sources of carbon. Methane will be formed in the initial pyrolysis of the heavier hydrocarbons such as ethane and propane; and natural gas contains an appreciable percentage of these heavier hydrocarbons (27). Methane is more stable at elevated temperatures than are the heavier hydrocarbons and consequently soot will not be precipitated easily.

For the carbon to transfer to the steel, the gaseous compounds must react with the steel which must be in the austenitic state. Carburizing is concerned with the solid solution of carbon in the austenite. The amount of carbon that can be taken into solution depends primarily upon the temperature and the composition of the steel.

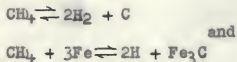
The carburizing process is a combination of two steps:

(1) Absorption of nascent carbon at the surface of the austenite.

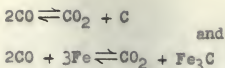
(2) Diffusion from the surface into the interior.

McQuaid (25) states that the carbon must be in the nascent or atomic form to be dissolved by the austenite. Carbon cannot enter into solution at the carburizing temperature if it is in the form of soot. Jominy (23) states that plain carbon steel will not be carburized by precipitated carbon until a temperature of 2300° F. is reached. The gas must form atomic carbon in the presence of austenite. If molecular carbon forms, it will interfere with the contact between the steel and the hydrocarbon gas.

With methane the carburizing reactions may be represented by the equations:



When carbon monoxide is present in the carburizing atmosphere, the following reactions at the surface of the steel may also be expressed as:



The carburizing reactions given above are quite complicated by the fact that the end products, CO_2 and H_2 , are, in the presence of water vapor, strong decarburizing agents. Therefore, in gas carburizing there are always two conflicting reactions occurring; one acting to carburize the steel the other acting to decarburize the steel. So that carburizing reactions may dominate, the carburizing atmosphere must be high in CO and CH_4 and low in CO_2 and H_2 .

After the carbon goes into solid solution as Fe_3C , it will tend to diffuse to zones of lower carbon concentration. The rate of diffusion of the carbon (or Fe_3C) increases with temperature provided a sufficiently high concentration of carbon is maintained at the surface.

Williams (36) gives three reasons for low penetrations:

- (1) Inaccurately measured temperatures.
- (2) Failure to measure case depth accurately.
- (3) Insufficient supply of active carburizing medium.

The initial carbon penetration is very rapid after there is some austenite at the steel surface (approximately 1350°F.); then the carbon gradient (27) is reduced by inward diffusion and the absorption of carbon from the carburizing medium drops. As the operating temperature is increased, the carbon penetration is also proportionally increased.

Two fundamental concepts of the mechanism of carburization are described by Harris in the Metals Handbook (27). The first concept deals with diffusion of the carbon in the gamma iron while the second concept considers factors that influence the transfer of atomic carbon from the carburizing medium to the steel surface.

Grossman (12) states that in pack carburizing, the carburizing compound influences the depth of case through its influence on the surface carbon content. He also states that in order to double the depth of case at a particular temperature the time must be approximately quadrupled.

Groves (13) states that the diffusion rate of carbon in austenite increases proportionately with carbon concentration and that the carbon demand of the steel surface is relatively great in the early stages of the carburizing process.

McQuaid (25) states that the diffusion of carbon in steel depends only on time and temperature, and the surface austenite can only dissolve additional carbon as diffusion inward reduces the carbon concentration at the surface below the equilibrium carbon content for a given steel at a given temperature. McQuaid also states that diffusion of carbon is independent of the carbon concentration at the surface. Therefore, time or temperature or both must be increased to increase carbon penetration. He states that a given steel will carburize at the same rate in a solid compound as it will in a gaseous atmosphere, if the temperature and time conditions are the same.

Meyer (18) states that a sufficiently high concentration of carbon must be maintained at the surface if the rate of diffusion is to be dependent upon the temperature entirely.

Frick's law of diffusion (27) states that the rate of flow of carbon from the surface of steel inward varies with the rate at which the carbon concentration varies with depth. This means that the characteristic of the concentration gradient determines the rate of flow of carbon in austenite at a given temperature. The gradient may be predicted when the carbon concentration at the surface of the steel is maintained consistently at a given temperature for a given time.

On the basis of carbon content, a case may fall into any one of three classifications: (1) hypoeutectoid, (2) eutectoid and (3) hypereutectoid.

The hypoeutectoid is one with carbon content below the eutectoid composition (about 0.85 percent carbon) and upon slow cooling, this case will show pearlite with excess ferrite.

The eutectoid case contains the correct amount of carbon so that upon slow cooling from the austenitic state to the pearlitic state, excess ferrite or cementite will not be present. For the alloy-type of carburizing steel the eutectoid point will be somewhat less than for plain carbon steels.

The hypereutectoid case has a carbon content in excess of the eutectoid composition. After slow cooling the structure will show pearlite and excess cementite.

By quenching in a suitable medium all three cases can attain a Rockwell hardness of over R_c 60.0 even though the carbon content may be above or somewhat below the eutectoid value.

The Ac_m line of the iron-carbon diagram (27) represents the solubility of carbon in austenite at various temperatures. The Metals Handbook (27) gives the approximately solubility of carbon in austenite for eight steels. With the addition of certain alloying elements, this line moves to the left on the iron-carbon diagram.

The case depth refers to that portion of the outer surface of steel articles that have been enriched with carbon above that of the original carbon content. The optimum case depth is dependent upon such factors as: (a) the service to which the part will be subjected, (b) the type of steel to be used, and (c) the amount of physical change in dimensions due to the formation of carbides.

Measuring case depth is a rather controversial subject according to the literature because case depth represents the depth of the hard wear resistant case that can be attained. The main obstacle is to obtain agreement on the point of demarcation between case and core. Two prevailing concepts are: the "effective depth" -- the perpendicular distance from the surface to the point where hardness is equivalent to Rockwell C50; "total depth" -- from the surface to the point where the carbon enrichment ceases.

Regardless of the process by which cases are produced, they are characterized by a transition zone in which the case blends into the core. This blending is no sharp line of demarcation. It is essential that the measurement be along a line normal to the outer surface.

The Metals Handbook (27) describes three methods of direct measuring:

- (1) Scale measurement of rough fracture.
- (2) Scale measurement of rough-polished cross section.
- (3) Scale measurement of highly polished cross section, using a high-power microscope. A cold nital etchant was recommended for specimens measured by the above methods.

The microscopical method is popular but it requires effort and time. A section is taken normal to the surface and is given the proper polishing and etching for viewing under a high-power microscope. The case and core can be studied with the steel in the hardened or slowly cooled condition. With the steel in the hardened condition, the carbon enrichment, distribution and condition may be studied to determine if the structure is all martensitic, partially martensitic plus retained austenite, or if the excess carbides are in solution. However, the demarcation between case and core is very difficult to determine. If the steel is slowly cooled it is possible to measure the case depth and to form an idea of the grain size of the structure.

A martensite-start method (29) is discussed in the transactions of the American Society for Metals.

Malcolm (24) believes that the most accurate and satisfactory method for determining the true case depth hardness is obtained by taper grinding a hardened specimen and taking hardness readings.

The taper ground surface is marked off at regular intervals and the hardness is determined at each point. The point on the ground surface where hardness readings become constant is noted as the point of maximum penetration of the case depth. Since such a study is slow and expensive the main application of this method has been in research work.

The accuracy of the taper grinding method decreases as the case depth decreases. The readings are also subject to error because of the softer metal beneath the case and great precision is required if dependable results are to be obtained.

CARBURIZING ATMOSPHERES

When gaseous atmospheres are used for the heat treatment of steel, there are five important chemical elements to consider. These elements are carbon, hydrogen, nitrogen, oxygen, and sulphur. From these elements, gaseous compounds of carbon monoxide (CO), carbon dioxide (CO₂), hydrocarbons, hydrogen, hydrogen sulphides, sulphur oxides, ammonia (NH₃) and water vapor may be formed.

Sulphur will cause scaling in low carbon or nickel bearing steels and discoloration in copper bearing non-ferrous metals.

If the gas contains sulphur it should be removed before it is used in any heat treating atmosphere.

Carbon dioxide and water vapor will react with ferrite and cause oxidation and decarburization. The reaction $\text{Fe}_3\text{C} + \text{CO}_2 \rightleftharpoons 3\text{Fe} + 2\text{CO}$ is reversible and in atmospheres where carbon dioxide is present, its effects may be neutralized by the addition of carbon monoxide. The ratio of CO and CO_2 has been worked out for steels at various temperatures (17). In the case of high carbon steel this ratio may be 100:1 or for low carbon steel 2:1.

Because water vapor has a very detrimental effect on carburizing, control of the dew point of the gas mixture used is essential. It has been found that small additions of ammonia, amounting to only 1 or 2 percent are beneficial in carburizing, probably because ammonia counteracts the effects of water vapor and carbon dioxide (28). Regardless of pre-drying processes, water vapor is always present in the furnace chamber because of the reaction of carbon dioxide with hydrogen as shown by the water gas reaction: $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$. The problem of obtaining a neutral or reducing atmosphere is solved by using definite proportions of carburizing gases such as carbon monoxide or methane to counteract the decarburizing gases. Carbon dioxide and hydrogen are both decarburizing in the presence of water vapor (7). The water reaction is reversible and results in an equilibrium situation of great importance.

At carburizing temperatures, carbon monoxide may be considered a carburizing gas. At high temperatures, carbon monoxide

is quite stable but at low temperatures it tends to break down and form carbon dioxide and soot.

Anhydrous ammonia is not found in a gas carburizing atmosphere ordinarily. However, a small addition of 1 or 2 percent is beneficial as ammonia counteracts the effects of water vapor and carbon dioxide. A process of simultaneous absorption of carbon and nitrogen may be desired in which case it is known as carbonitriding (28). Many claims for carbonitriding have not been substantiated and there is contradiction in the literature.

The hydrocarbons such as methane, propane, ethane and butane are carburizing gases. At elevated temperatures they dissociate into carbon and hydrogen and if the percentage of hydrocarbons in a carburizing atmosphere is not carefully controlled, excessive soot precipitation will result during dissociation. The general tendency, since soot formation is usually not desirable, is to use the hydrocarbons as a source of a balanced composition of CO and CO₂, by partial combustion with air generally over a catalyst.

In current carburizing practice, outside generator prepared "carrier" gases are commonly used. The gases produced are nearly neutral and are used as the diluent for the hydrocarbons. The Holcroft Company (20) has developed a furnace which does not use an outside generator. For the carrier gas they utilize the spent gases from the exhaust by recirculating them and adding necessary enriching hydrocarbons.

A carrier gas (21) serves to:

- (1) Purge the furnace.
- (2) Provide positive pressure in the carburizing chamber.
- (3) Dilute the active hydrocarbons enough to prevent soot precipitation on the work and furnace.

Purging consists of displacing the existing atmosphere in the furnace, with the carrier gas, as small amounts of oxygen will react with the hydrocarbon gas to form carbon dioxide and water. A purging formula (16) appeared in 1945:

$$t = 0.69 \quad K \frac{V}{F}$$

where

t = Half-life period in minutes.

F = Flow of carrier gas in cu. ft. / hr.

V = Volume of retort in cu. ft.

K = Temperature factor.

$$= \frac{\text{Temp. of supply gas in } ^\circ \text{F.} - 460}{\text{Temp. of retort gas in } ^\circ \text{F.} - 460}$$

Therefore, the higher the temperature of the retort the shorter is the purging time for a given flow and volume. After properly purging, a positive gas pressure must be maintained inside the furnace and be sufficient to prevent any air infiltration.

Carrier gases have different analyses depending on the method of generation (22). An important function is serving as a vehicle for the active carburizing gas such as methane or propane, and thus making up most of the volume of the mixture in the furnace. Exothermic gas generators utilize an air-gas mixture which

is burned in a combustion chamber, after which the products of combustion are passed through drying devices for the removal of water vapor. The most widely used endothermic gas generators utilize an externally-heated retort filled with nickel-coated brick to serve as a catalyst. This generator operates with air-gas mixtures and a gas of constant analysis can be maintained.

One of the earliest endothermic generators (22) utilized an externally-heated retort filled with charcoal through which a metered amount of air was passed. The chemical reaction involved in this generator is: $C + 1/2 O_2 + 2N_2 = CO + 2N_2$. This generator gas analyzes approximately 67 percent N_2 , with the remainder CO and CO_2 . Since the only source of hydrogen is the water vapor in the input air, hydrogen and water vapor contents are very low. The CO and CO_2 contents of the gas are determined by the reaction temperature, the CO increasing and CO_2 decreasing with temperature increases.

With some endothermic gas generators, air-gas mixtures or products of combustion are passed through a charcoal retort instead of passing air alone. The resulting atmosphere gases have higher hydrogen contents, but are otherwise the same as if only air was passed through charcoal in an endothermic generator, since heated charcoal reduces highly oxidizing components.

Frischman (8) states that one of the first carrier gases introduced in the 1930's, was a mixture of one part natural gas to eight parts air burned to incomplete combustion in a chamber

without the application of external heat. This was an exothermic reaction with a gas composition of the following percentage:

9.0 - CO_2

3.0 - CO

1.0 - H_2O

Balance - N_2

To overcome the decarburizing nature of the gas, 50 percent natural gas was added which then gave a composition of the following percentage:

9.6 - CO

0.0 - CO_2

0.2 - O_2

25.2 - H_2

27.4 - CH_4

Balance - N_2

There were objections to the use of this mixture because soot precipitated on the work and in the retort.

An improved gas was then prepared endothermically by using one part natural gas to two and one-half parts air in the endothermic reaction chamber. To this carrier gas was added the hydrocarbon gas but the methane content was still too high for producing clean work.

By using catalysts, it is now possible to produce a carrier gas virtually free of methane. A typical composition of this gas produced at 1850°F . is given by the following percentages:

20.6 - CO

42.0 - H₂

0.0 - O₂

0.0 - CO₂

0.8 - CH₄

Balance - N₂

Dew point - 0° F.

By adding 12 percent natural gas to this carrier gas the composition then has the following percentages:

17.6 - CO

43.9 - H₂

0.0 - O₂

0.0 - CO₂

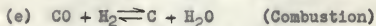
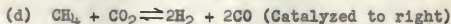
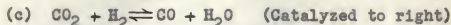
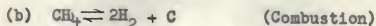
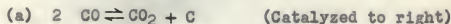
7.6 - CH₄

Balance - N₂

Dew point - -17° F.

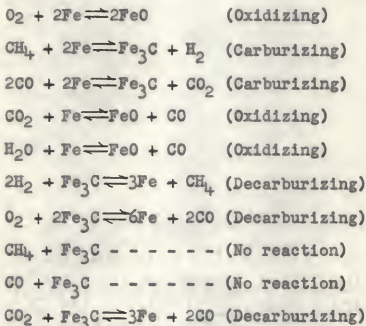
When using combustible atmospheres there is always an explosion hazard. Smith (31) states that if a special atmosphere has a concentration exceeding 8.8 percent of flammable incomplete products of combustion it will enter the explosive range when mixed with air. Explosive mixtures are most likely to occur during starting up or shutting down while the air in the furnace is being replaced with a flammable atmosphere or with air. The possibility of explosion is avoided if all parts of the reactor are above the gas ignition temperature of 1400° F. which is generally reliable.

The fundamental gas reactions (36) of importance in gas carburizing are:



The direction of these reactions are dependent on the ratio of gases, the temperature, and presence of catalysts. The steel surface to be carburized and the retort material will exert definite effects. Thus, the composition of the atmosphere is dependent upon several factors and it can be seen that the atmosphere and the reactions are quite complex. The Metals Handbook (27) gives the results of a study of the reactions (a) and (b), based on equilibrium constants. This discussion assumed that reactions (a) and (b) proceed until they are in equilibrium with the austenite at the surface of the steel. It was stated that experimental data showed that the concentration of methane in an atmosphere must be many times the concentration that would be in equilibrium with the atmosphere. If it does not do this, it will change rapidly in composition until the gas mixture and the steel surface come close to being in equilibrium. If these reactions are on the decarburizing side, they may determine the effect of an atmosphere, even though it has a high methane content. Williams (36) indicates that carbon monoxide is relatively feeble, unless

high flows are used. Its reaction as a carburizing agent is overshadowed by small amounts of hydrocarbons. Since the controlled carburizing atmosphere problem involves the effect of H_2 , O_2 , CH_4 , CO , CO_2 , and H_2O separately or in combination with the iron and carbon of the steel (10), consideration must be given to the following reactions:



The rates of the reactions that involve Fe_3C are affected by the carbon content of the work; while all the rates will depend on the rate of supply of gas to the surface.

The equilibrium of the gases CO and CO_2 ; H_2O and H_2 ; CH_4 and H_2 with austenite saturated with carbon at different temperatures have been worked out with fair agreement and have been summarized by Stansel (32).

Plate I shows Stansel's curves which are based on equilibrium with austenite saturated with carbon at any particular temperature. Equilibrium curves for unsaturated steels are available in the literature.

The area between curves "B" and "C" above the point of intersection is not a scaling condition but is decarburizing. Below this point is where oxidation and carburization are indicated to occur simultaneously. However, at this temperature, carburizing is very slow if it occurs at all. There is a decarburizing action upon cementite by H_2 , and possibly CO_2 , however, the CH_4/H_2 carburizing curve ends at the A_{C1} point of the iron carbon diagram.

The curves show for a particular temperature, a water vapor atmosphere whose oxidizing tendency is balanced by H_2 will result in oxidation if the temperature is lowered. Thus, the water vapor must be very limited if the charge is to be cooled in the furnace. Any ratio of CO and CO_2 (curve "C") that is not oxidizing at a high temperature will not be oxidizing at a lower temperature. Stansel's curves show that water vapor, or CO_2 , unbalanced by a reducing gas, will be oxidizing at any heat-treating temperature. The two curves "C" and "D" represent the water gas reaction. Both H_2O and H_2 in curve D are decarburizing and small amounts of these gases merely increase the range of no scaling but the gas is decarburizing.

Curves "B" and "C" indicate that a higher ratio of CO to CO_2 is required to prevent decarburization than is required to prevent scaling.

High methane concentrations have a bearing on the deposition of soot and is increasingly unstable at higher temperatures. Hydrogen, in appreciable amounts, tends to counteract this. The

CO_2/CO ratio is also directly related to the deposition of soot. An excessively high ratio of CO to CO_2 at any given temperature favors sooting. Since CO is more stable at higher temperatures, this sooting tendency decreases with temperature increases.

Groves (13) describes how the dew point and percent of carbon monoxide of a carburizing atmosphere may be employed as a control check. He states that although the ratio of CO_2/CO and $\text{H}_2\text{O}/\text{H}_2$ in the furnace atmosphere determines the equilibrium carbon concentrations, a simple CO_2 or dew point check may generally be adequate for production control.

EXPLANATION OF PLATE I

Stansel's curves which are based on equilibrium with austenite saturated with carbon at any particular temperature.

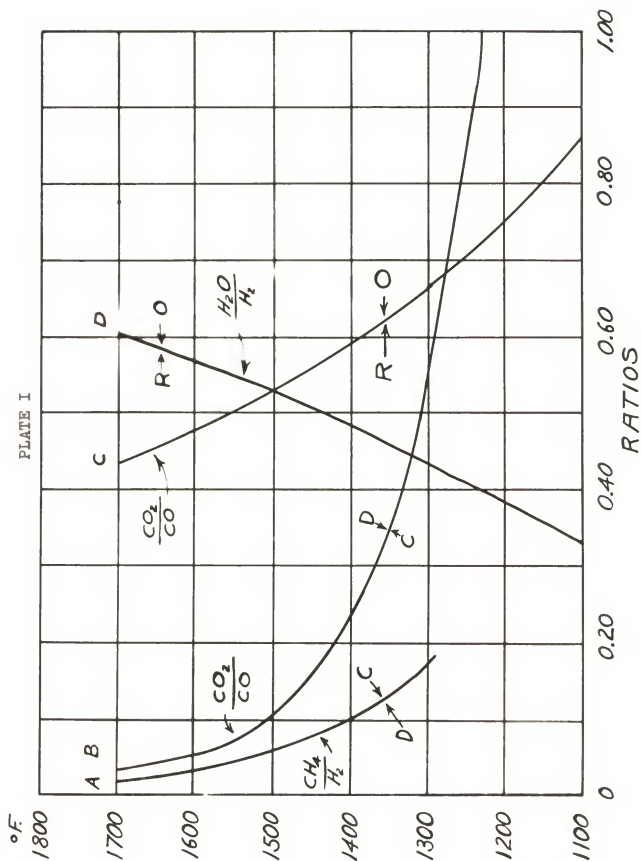
D - - - Decarburizing area

C - - - Carburizing area

R - - - Reducing area

O - - - Oxidizing area

PLATE I



APPARATUS AND EQUIPMENT

The apparatus was set up according to the schematic diagram of Plate II. As the air supply was quite wet, it was dried by being passed through a chamber containing calcium chloride, after which the dew point was -15° F. A pressure reducing gauge of the oxy-acetylene welding type was used to lower the 90 pound line pressure to a working pressure for the flow meter. A mercury manometer was used to aid in setting the reducing gauge so that the range of the particular flow meter tube could be used. Bunsen burner valves were adapted and arranged on a panel for the control of the rate of flow of the air and gas through the flow meters. The flow meters used were Type 130-BH, manufactured by the Fischer and Porter Company of Hatboro, Pennsylvania. With four calibrated tubes and six floats, a flow range of 5 to 38,000 cc per minute was available. A complete set of charts for determining the tube scale reading for a given flow was provided by the manufacturer with the set of tubes, floats, and mounting bracket. After leaving the flowmeter, the air flowed to the charcoal tube of the carburizing unit where it was mixed with the incoming natural gas.

The Kansas Power and Light Company of Manhattan, Kansas, supplied the natural gas which had a nominal analysis of:

CH_4 - - - 78.0 percent

C_2H_6 - - 11.75 percent

CO₂ - - - Trace
O₂ - - - None
Resid. - 10.25 percent
H. V. - - 995 B.t.u./ft.³
Dew Point - Below -30° C.

Because the dew point was quite low, the gas was not further dried. With the line pressure being only 1.7 inches of mercury, a pressure reduction valve was not required. From the flow meter, the gas flowed to the charcoal tube. Here, the gas and air were mixed by flowing through a "Y" in the rubber stopper of the charcoal tube. This mixture then flowed down through the charcoal tube and into the carburizing retort. After serving its purpose in the retort, the atmosphere flowed out through a short pipe at the top of the unit. The exhausted gases were burned to dispose of the carbon monoxide and methane and to serve as a visual indication of the carbon richness of the carburizing atmosphere.

The carburizing retort was placed vertically in a resistance wire (chromel "A") wound electric furnace. The temperature of the retort was controlled by using a Model 3224 Wheelco pyrometer of the Wheelco Instrument Company of Chicago, Illinois. The temperature thermocouple was of chromel-alumel and was protected from the retort atmosphere by using an inconel tube.

The transformer for the furnace was equipped with several plug-in points so that the optimum operating voltage could be found.

A Type PM-1 Thwing potentiometer of the Thwing-Albert Instrument Company of Philadelphia, Pennsylvania, was used for checking the accuracy of the Wheelco pyrometer. This instrument is completely thermo-electric pyrometers.

The carburizing retort shown on Plate IV was constructed of 16 gauge inconel. Inconel is a high nickel alloy (approximately 73 percent Ni., 15 percent Chromium, balance iron). This alloy was used as it has strength and high corrosion resistance at elevated temperatures. Inconel can withstand repeated heating and cooling in the range 0-1700° F. without incurring brittleness. All tubes extending down into the retort from the retort cover were of inconel. Plate V shows a cross sectional view of the carburizing apparatus. A fan of one inch diameter served to circulate the gases within the retort so as to insure a homogeneous mixture throughout and to prevent uneven carburization. The fan and shaft were made of 18-8 stainless steel. Due to intercrystalline corrosion, the fan had to be replaced once during the series of experiments. The fan was driven by a small motor at the rate of 1750 r. p. m. A packing gland containing asbestos string impregnated with graphite was used to prevent the leakage of gases around the shaft. A block of graphite was imbedded in the refractory to serve as a bearing.

The cover of the retort fitted into a flange of the retort which was filled with a fine grain sand. The purpose of this sand seal was to provide for an easy method to remove and replace the cover assembly and to prevent the inward permeation of air.

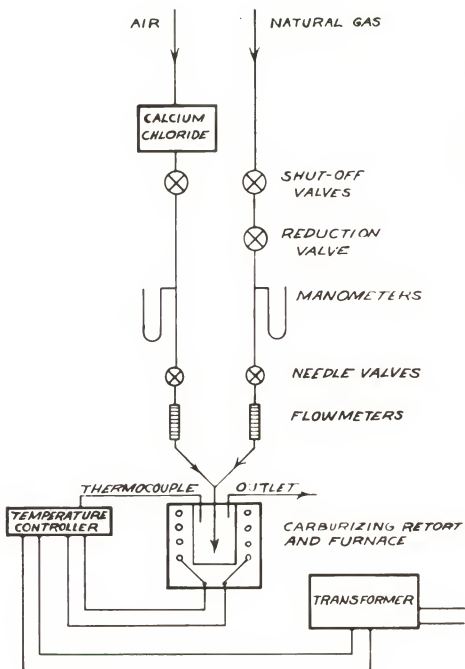
A slight pressure of the atmosphere within the retort served to prevent this inward permeation. The refractory of the cover rested directly upon the sand seal.

Alundum refractory was cast within the cover and around the tubes. A hole was drilled through it for the fan shaft. Expanded metal was welded within the cover to serve the purpose of reinforcing the refractory. The refractory extended down one inch from the top of the retort to prevent undue heat loss.

The charcoal tube was provided with two outlet holes at the bottom. The gas mixture flowed down through the hot charcoal and out these holes near the bottom of the retort. This maximum length of travel provided for heating of the gases, combustion, and reaction with the hot charcoal before entering the retort to serve as a carburizing atmosphere.

EXPLANATION OF PLATE II

A schematic diagram of the gas carburizing
apparatus and equipment.

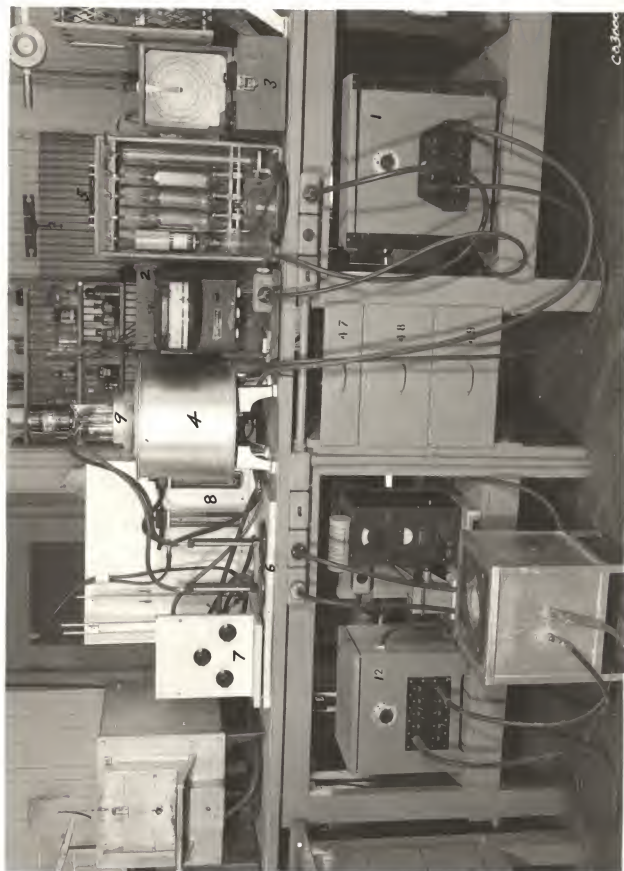


EXPLANATION OF PLATE III

Gas carburizing apparatus and equipment

- (1) Transformer
- (2) Temperature controller
- (3) Potentiometer
- (4) Furnace
- (5) Burrell gas analyzer
- (6) Flow meters
- (7) Bunsen burner valves
- (8) Manometers
- (9) Carburizing unit

PLATE III



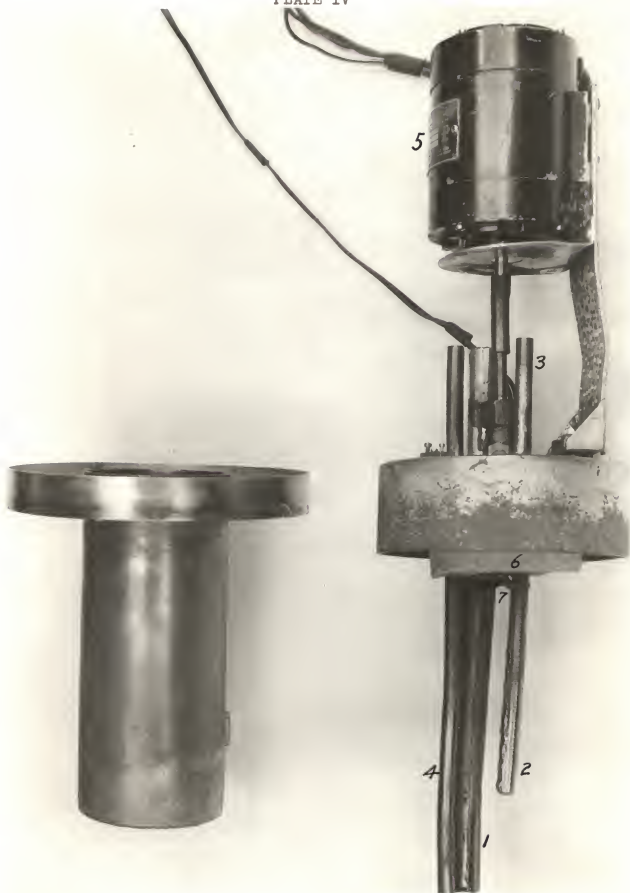
EXPLANATION OF PLATE IV

Figure 1. Inconel retort with sand seal flange

Figure 2. Retort cover assembly

- (1) Charcoal tube
- (2) Thermocouple tube
- (3) Short outlet tube
- (4) Long outlet tube (not used)
- (5) Motor
- (6) Alundum refractory
- (7) Fan

PLATE IV

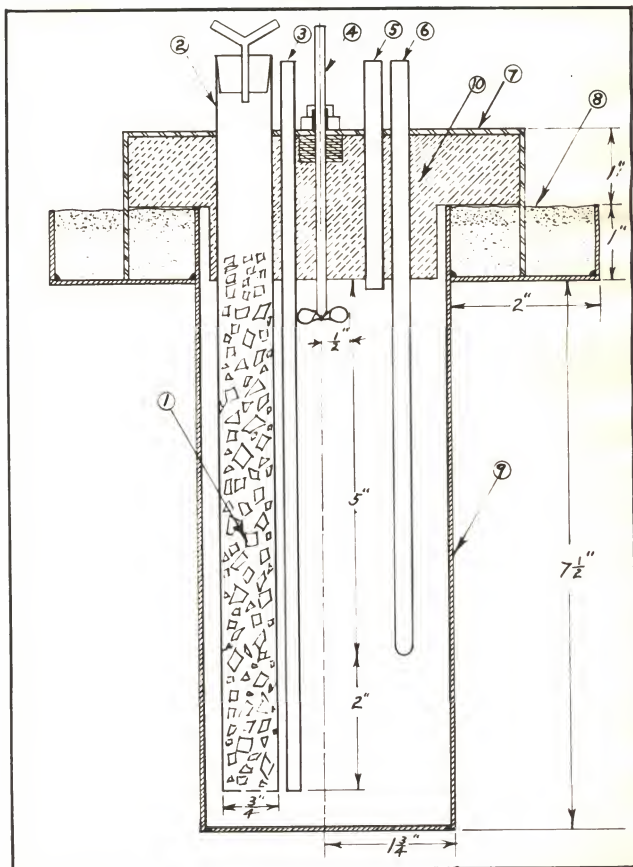


EXPLANATION OF PLATE V

A cross sectional view of the carburizing unit showing the arrangement of the tubes within the retort

- (1) Charcoal
- (2) Charcoal tube
- (3) Experimental inlet and outlet tube
- (4) Fan and shaft
- (5) Short outlet tube
- (6) Thermocouple tube
- (7) Retort cover
- (8) Sand seal
- (9) Carburizing retort
- (10) Alundum refractory

PLATE V



EXPERIMENTAL PROCEDURE

Refined technique by the furnace operator is of utmost importance since poor results may often times be traced to improper or careless operation. In establishing the procedure, standards were established and variables were reduced to a minimum in order to assure the validity of the results.

A sample of S. A. E. 1117 steel, (approximately 0.17 percent carbon) was used as the specimen to be carburized. The specimen was 3/8 inch in diameter by approximately 2 inches in length and was cleaned and polished to a bright finish by using a fine grain polishing paper. Care was exercised to keep the specimen free from grease and water. Only one specimen was in the retort during a carburizing period and it was hung between the charcoal tube and the thermocouple tube with chromel wire so the bottom of the specimen was even with the bottom of the thermocouple tube.

Twelve grams of charcoal (1/4 inch particles) were predried in an oven at 300° F. for a period of at least fifteen minutes. The charcoal was not put in the charcoal tube until the furnace was at the carburizing temperature (1600, 1675, or 1750° F.). When the desired temperature was reached and the specimen was placed in the retort the gas or air-gas mixture was adjusted for the desired flow rates. By this procedure the hazard of explosion was practically eliminated as the retort temperature was

considerably above the gas ignition temperature of 1400° F. The beginning of the carburizing run was recorded after a purging time of approximately five minutes. The author believed that this time was sufficient to rid the retort of air which would retard the carburization. After the rates of flow were adjusted the circulating fan was started and it ran during the entire carburizing period.

Before and during each carburizing period the temperature controller was standardized and periodically it was checked for accuracy by using a Thwing potentiometer.

The flowmeters were checked periodically during the carburizing period for continuation of the original scale setting.

After approximately one hour the gas analysis of the atmosphere was made. The gas sample was taken directly from the exhaust tube and it flowed through rubber tubing to the Burrell Orsat type gas analyzer. After taking the gas analysis, the same tubing was used for conveying the gas to a test tube device (Plate VI) for determining the dew point of the carburizing atmosphere. One gas analysis and one dew point determination were made for each carburizing period. At the end of the carburizing period the furnace and fan were turned off. The outlet was then closed to prevent infiltration of air and the gas and air lines were immediately closed by using pinch cocks on the rubber tubing.

The specimen was thus allowed to slow cool in the furnace which brought out the soft pearlitic structure. The existing carbon potential of the atmosphere at the time of shut down was

sufficient during cooling to prevent decarburization. The sand seal appeared to be quite effective and permeation of gases through it was not sufficient to cause any deleterious effects. Depending upon the carburizing temperature, the retort cooled down to 1350° F. in approximately fifteen minutes.

The excess charcoal was removed, weighed and recorded. The amount of sooting in the retort, on the tubes and specimen was noted and recorded. The retort and tubes were then cleaned with a wire brush to remove any soot which was deposited.

METHODS OF ANALYSIS

Dew Point Determination

After approximately one hour from the beginning of the carburizing period a dew point was taken of the carburizing atmosphere.

Plate VI shows an arrangement of two test tubes, inlet and outlet tubes and a rubber stopper. The rubber hose from the exhaust pipe was connected to the long metal tube which extends from the rubber stopper at a 45° angle. Since this tube extends to the bottom of the large test tube, the gas is thus caused to flow over the small test tube before it exhausts. Approximately one inch of ethyl alcohol was placed in the small test tube. Into the alcohol was dropped small pieces of dry ice (1/4 inch pieces) which caused the temperature of the alcohol to drop. By placing the bulb of a thermometer in the alcohol the temperature

at which dew first formed on the small test tube was noted and recorded as the dew point. As the small test tube was thin walled, the author believed that the lag of the dew point, because of the heat transfer through the glass, to be insignificant for this experimental work.

Gas Analysis

A Burrell Cabinet Model VT gas analysis apparatus was used for determining the carbon monoxide, carbon dioxide, methane and hydrogen contents of the furnace atmosphere. The apparatus had absorption pipettes for determining the oxygen and carbon dioxide contents and a catalyst tube in which catalytic oxidation took place for the determination of combustible gases. The Burrell catalog (3) describes the complete procedure for operating the apparatus. The gas analysis for each carburizing run was taken approximately one hour after the carburizing temperature was reached. After the analysis, the results of the analysis were checked by totaling the components of the atmosphere.

Case Depth Determination

The slow cooled specimen was sectioned at right angles to the surface by using an abrasive cut-off wheel. The specimen was then mounted in plastic and polished. Cold nital was used as the etching reagent.

A metallograph was used in the determination of the case depth of the test specimens. By using an eyepiece equipped with

a scale graduated in thousandths of an inch and with a magnification of 100X, a ground glass screen was calibrated so as to give the case depth directly in thousandths of an inch.

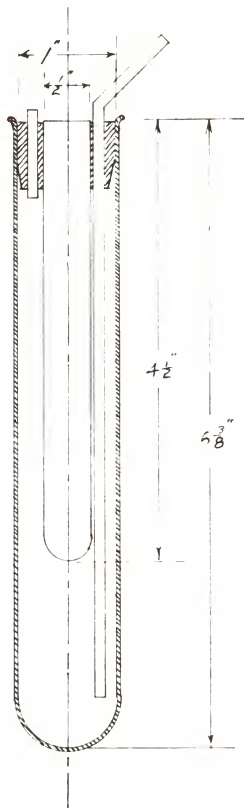
The plastic mounted specimen was then placed on a glass platform over the objective lens of the metallograph. The plastic served to hold the specimen over the lens in the proper position as well as to support the edges of the metal during the polishing procedure.

The image of the microstructure was projected to the ground glass screen and a direct reading in thousandths of an inch was taken at three equally spaced positions on the cross section of the case. An average of these three readings was recorded at the case depth.

The division line between the core, hypoeutectoid, eutectoid, and hypereutectoid zones was established where a marked change in the amount of cementite (Fe_3C) appeared. Figure 3 illustrates the three zones in a carburized specimen with a hypereutectoid case. This particular specimen had a total case depth of 0.046 inch which was obtained in three hours carburizing time at 1750° F.

EXPLANATION OF PLATE VI

Apparatus for determining the dew point of the
carburizing atmosphere



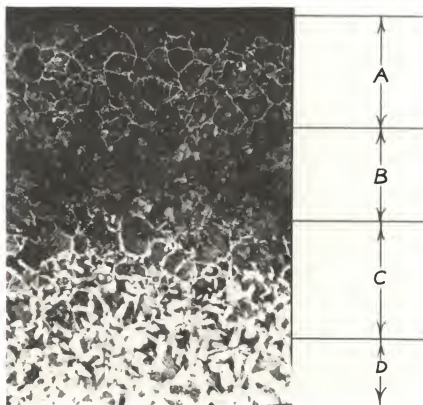


Figure 3. The zones in a carburized specimen

A - Hypereutectoid

B - Eutectoid

C - Hypoeutectoid

D - Core

DISCUSSION OF RESULTS

This research problem approached with the objective of producing a gas carburizing unit that would work without an outside generator for the preparation of a "carrier" gas. The design and cost of construction were also of importance in consideration of the original purpose of this problem. The design was formulated with the idea of utilizing the same furnace for the preparation of the carburizing atmosphere as well as for the actual carburizing process. The charcoal served quite well in controlling the dew point as well as to reduce any decarburizing gases entering the retort.

The carburizing retort and the tubes of the cover assembly were made of inconel because of its excellent high temperature physical properties and corrosion resistance. All joints were heli-arc welded. It was noted that if there were any blow holes or slag inclusions where carbon might enter, failure would first begin at those points. The carbon enters at high temperature, is entrapped during cooling and then causes a crack to develop. This happened several times on the welds of the tubes.

The sand seal served effectively against inward permeation of air since there were no noticeable deleterious effects that might have been due to leakage through the sand seal.

The fan was necessary to keep the atmosphere in motion so as to insure adequate distribution of the hydrocarbon gas. This atmosphere distribution was necessary if even case depths were to be obtained and it also assured more even heating. Before the fan was placed within the retort, very noticeable irregularities of case depth were observed.

After an estimated 800 hours of service at or near the carburizing temperature, the inconel retort and tubes appeared to be in very excellent condition structurally.

With undiluted natural gas, the charcoal and inconel tubes collected some of the precipitated soot from the dissociation of the natural gas. The only advantage of this was that less soot was deposited on the walls of the retort and on the specimen. For two-hour carburizing periods undiluted natural gas gave an average case depth of 0.045 inch with approximately 0.012 inch hypereutectoid. There appeared to be no difference in the case depth or case characteristic if charcoal was or was not used. When only natural gas was used, with or without charcoal, the soot which formed was hard and probably became more impenetrable with longer carburizing periods.

When air and gas were used without charcoal in the tube, the resulting atmosphere had a dew point so high that the concentration of natural gas in air mix had to be so high that the result was excessive sooting. Carburizing was obtained but there was no control of the dew point.

It was obvious that a diluting gas was necessary to control the sooting and the case characteristics. By using air only, at the rate of 200 cc/minute, the charcoal reduced the oxygen and water vapor and gave an atmosphere of the following composition:

CO - - 18.0 to 19.7 percent

CO₂ - 0.23 to 1.10 percent

H₂ - - Trace

N₂ - - Balance

Dew point -15° C.

Since the only source of hydrogen was in the water vapor in the input air, hydrogen and water vapor contents were quite low. The CO and CO₂ contents of the atmosphere is determined by the reaction temperature, the CO increasing and the CO₂ decreasing with increasing temperature.

With a mixture of air and gas passing through the charcoal, the resulting atmosphere had a much higher hydrogen content. Table 1 gives the varying compositions for various ratios of air to gas through the hot charcoal. There seemed to be somewhat of a lack of correlation between the case depth and the percentage of CH₄ and CO; however, there was good correlation between the case depth and the percentage of CO₂ and water vapor. The amount of sooting appeared to increase with the percentage of methane in the atmosphere. The CO and CO₂ contents were essentially the same, since heated charcoal reduces oxidizing

gases and there was always an excess of charcoal. The amount of charcoal consumed during each condition shows that this cost item of the operation is quite low. With a suitable ratio of air and gas through the charcoal very little soot was deposited within the retort. No soot at all was deposited on the specimens which were carburized by using air-gas ratios of 200:75 and 300:275 cc/minute. There appeared to be a range of 20-60 percent gas in air mix which would give good carburizing with the minimum of sooting. The case depths for varying temperature and time for these ratios are shown in Figures 4 and 5. The photomicrographs of Plates VII, VIII, IX, X, XI, and XII show the corresponding cases for the curves of Figures 4 and 5. For corresponding temperature and time the case depth was generally deeper for the richer gas ratio. It was observed that the carbon richness of the atmosphere influences the color of the flame of the exhausting gases to the degree that a carburizing or decarburizing atmosphere can usually be distinguished. With the higher carbon potential, the flame was orange in color.

For like operating conditions, it was observed that for low flow rates, uneven case depths were likely to result. This was believed to be due to insufficient circulation caused by the fan being too small. If flow rates were too high, uneven cases were also likely to result. However, with the higher flow rates, uneven case depths were not nearly so noticeable. In general, a flow rate which will give approximately one complete retort change per minute is most desirable. The increase

in volume of the heated gases was used in establishing this rate of change. However, the flow rates given in Table 1 are the rates for air and gas at standard conditions.

The photomicrographs show the lack of hypereutectoid composition by using the low gas mixture while a great amount of hypereutectoid resulted from the richer gas mixtures, especially at the higher temperatures.

For corresponding conditions, all curves except No. 1 of Figure 4 agree reasonably well with the carburizing data presented by Harris (15)

From the data obtained, it is believed that this procedure for producing a desirable and effective carburizing atmosphere can be perfected so that the surface carbon and the carbon gradient can be varied to meet any ordinary commercial requirement. Possibly a reliable procedure for reducing the proportion of natural gas, during the latter stages of the carburizing period could be worked out. This would allow the carbon to diffuse inward and also reduce the tendency of soot formation during the latter stages of the carburizing period.

Successful results depend as much upon correct operating procedures as well as upon the carburizing unit.

Table 1. Gas carburizing data sheet.

men no.	: Carb. : time	: Flow : in cc/min.	: Charcoal : consumed	: Dew : point	Gas analysis				: Case depth-inches	: Sooting : Conditions					
					: CO	: H ₂	: CH ₄	: CO ₂							
: Specimen : Carb. : Flow rates : Charcoal : Dew : Case depth-inches : Sooting : Conditions															
: men : no. : : Carb. : time : in cc/min. : consumed : : point : : Hyper. : Eutect. : Hypo. : : Conditions															
: :															

Table 1. (cont.)

Specimen no.	Carb. temp. : Of.	Carb. time : hrs.	Flow rates : Gas : Air	Charcoal consumed : in cc/min.	Gas analysis			Dew point : °C.	Case depth-inches		Sooting Conditions
					CO	H ₂	CH ₄		Hyper.	Eutect.	
138	1675	2	175	300	5.0	15.3	33.3	5.7	19	-	Light
139	1675	2	225	300	4.85	12.6	37.2	6.1	21	.009	Light
140	1675	2	225	300	4.72	12.0	37.2	6.1	21	-	Light
141	1675	2	275	300	4.74	16.2	35.0	3.9	nil	-	Light
142	1675	2	275	300	4.82	13.0	43.0	3.1	11	-	Light
143	1675	2	100	50	0.80	15.6	51.6	0	nil	-	Light
144	1675	2	150	50	1.97	15.7	39.2	0	nil	-	Light
145	1675	2	150	50	0.20	1.4	57.4	10.2	nil	-	Light
152	1600	1	275	300	3.41	14.4	40.8	3.1	20	-	Light
154	1600	2	275	300	5.57	12.5	39.2	4.9	20	.007	Light
153	1600	3	275	300	6.16	10.6	36.4	7.6	40	.008	Medium
156	1600	4	275	300	6.22	18.7	40.3	1.5	40	.011	Medium
155	1600	5	275	300	5.99	14.5	40.1	3.5	nil	-	Heavy
149	1675	1	275	300	2.47	12.0	39.0	5.4	nil	-	Very light
146	1675	1	275	300	3.22	12.8	38.7	5.4	nil	-	Medium
151	1675	2	275	300	5.00	12.0	31.6	8.4	nil	.008	Medium
147	1675	3	275	300	6.26	10.3	40.5	6.3	nil	.010	Medium
177	1675	3	275	300	5.70	9.3	28.5	8.7	24	.013	Medium
148	1675	3	275	300	5.63	10.5	45.5	2.3	19	.010	Heavy
150	1675	5	275	300	7.00	16.3	31.3	4.1	nil	.018	Heavy
175	1750	1	275	300	3.10	6.8	12.8	12.6	50	-	Medium
176	1750	2	275	300	4.80	10.6	34.8	8.1	nil	.013	Medium
172	1750	3	275	300	3.70	7.4	28.0	10.0	nil	.011	Medium
173	1750	4	275	300	6.10	7.6	27.6	11.8	nil	.017	Medium
174	1750	5	275	300	7.00	8.7	22.8	10.6	25	.021	Heavy
162	1600	1	75	200	2.41	16.1	18.0	6.7	38	.033	Heavy
163	1600	2	75	200	4.8	17.1	15.7	7.1	58	-	Very light
170	1600	3	75	200	4.2	13.5	6.3	10.9	60	-	Very light
179	1600	4	75	200	5.16	12.0	15.2	6.9	60	.013	Light
165	1600	5	75	200	4.85	15.3	11.0	6.0	40	.009	Light
166	1600	5	75	200	6.55	14.0	13.2	8.7	79	.010	Light
159	1675	1	75	200	3.41	20.7	24.4	3.4	21	.005	Very light

Table 1. (cont.)

no.	Speci- men	: Carb. : temp.	: Carb. : of	: Flow rates : time in : cc/min.	Charcoal: consumed:	Gas analysis			: Dew : point:	Case depth-inches			: Sooting : Conditions
						: CO	: H ₂	: CH ₄	: CO ₂	: OC	: Hyper.	: Eutect.	: Hypo.
178	1675	1	75	200	3.18	13.8	20.8	9.5	.43	-1	-	.007	.010
179	1675	2	75	200	4.14	21.8	28.6	2.5	.40	-5	-	.013	.014
180	1675	3	75	200	5.88	15.6	26.2	4.4	.40	-3	-	.013	.013
181	1675	4	75	200	5.50	21.3	26.2	5.3	.37	-2	-	.018	.013
182	1675	5	75	200	5.31	17.7	27.0	3.5	.39	-6	-	.022	.022
183	1675	1	75	200	4.26	12.1	17.3	9.1	nil	-4	-	-	.019
184	1750	1	75	200	3.62	18.0	24.1	4.9	.40	-3	-	.010	.010
185	1750	2	75	200	5.0	15.1	18.3	7.5	.40	-1	-	.012	.016
186	1750	2	75	200	5.48	18.2	24.0	3.5	nil	0	-	-	.036
187	1750	3	75	200	4.6	17.0	22.2	4.5	nil	-4	.012	.015	.018
188	1750	3	75	200	4.89	12.0	18.0	8.5	nil	-4	-	.021	.022
189	1750	3	75	200	5.25	14.9	17.8	8.6	.30	-2	-	.016	.022
190	1750	4	75	200	6.75	19.0	23.6	3.7	nil	-1	-	.025	.035
191	1750	5	75	200	6.16	17.7	23.8	4.0	nil	-3	-	.047	.035
192	1675	1	222	None	None	0	69.5	6.2	nil	-7	-	.012	.011
193	1675	2	222	None	None	0	69.0	6.5	nil	-7	.011	.012	.013

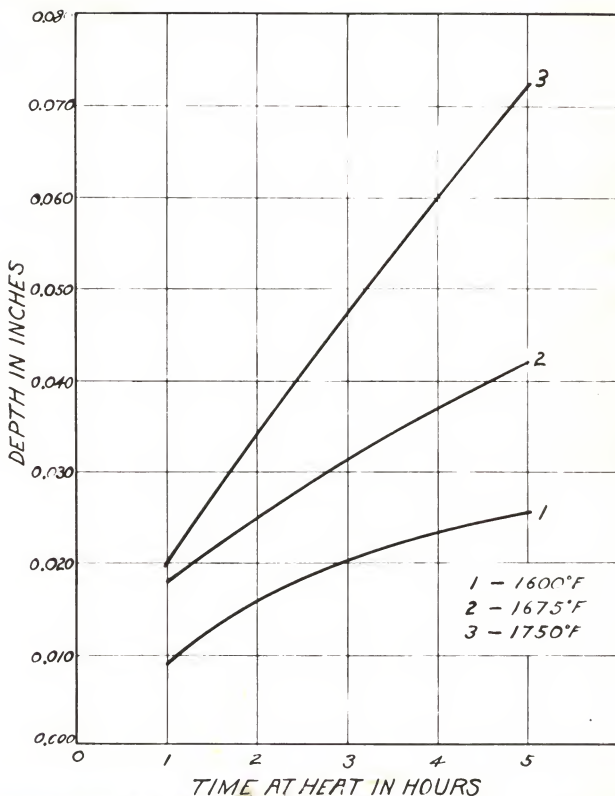


Figure 4. Total penetration at specified times and temperatures using an air-gas ratio of 200:75 cc/minute through charcoal

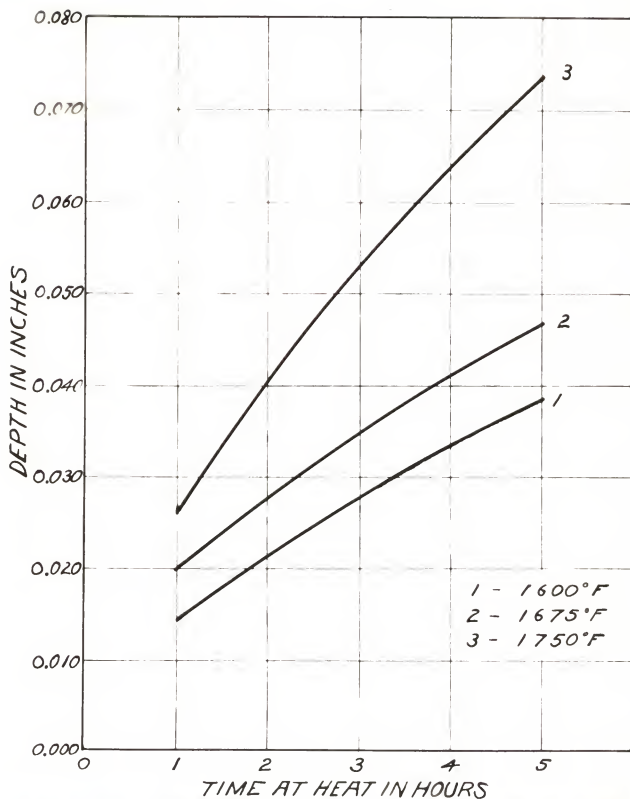


Figure 5. Total penetration at specified times and temperatures using an air-gas ratio of 300:275 cc/minute through charcoal

EXPLANATION OF PLATE VII

S. A. E. 1117, carburized at 1600° F. in an atmosphere prepared from an air-gas ratio of 200-75 cc/minute through hot charcoal and cooled slowly in the retort. (Etched with 2 percent nital.) X100.

	Time in hours	Case depth in inches
Figure 6	5	0.024
Figure 7	4	0.023
Figure 8	3	0.021
Figure 9	2	0.014
Figure 10	1	0.009

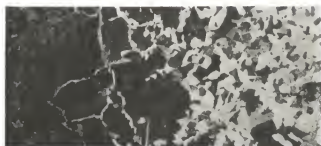


Figure 6



Figure 7



Figure 8

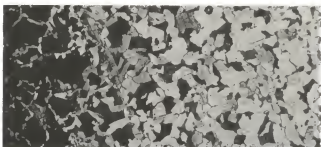


Figure 9

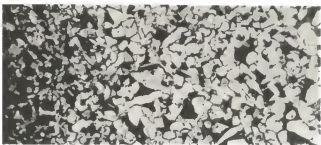


Figure 10

EXPLANATION OF PLATE VIII

S. A. E. 1117, carburized at 1675⁰ F. in an atmosphere prepared from an air-gas ratio of 200-75 cc/minute through hot charcoal and cooled slowly in the retort. (Etched with 2 percent nital.) X100.

	Time in hours	Case depth in inches
Figure 11	5	0.044
Figure 12	4	0.031
Figure 13	3	0.028
Figure 14	2	0.027
Figure 15	1	0.018

PLATE VIII

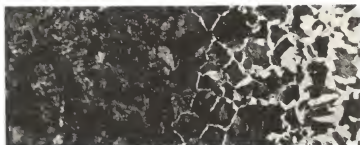


Figure 11

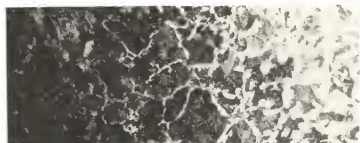


Figure 12

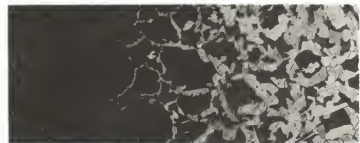


Figure 13

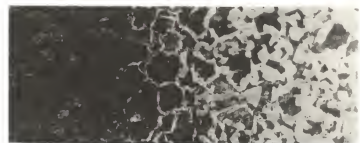


Figure 14

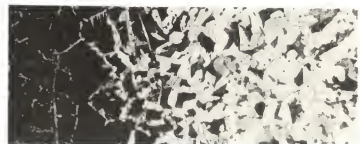


Figure 15

EXPLANATION OF PLATE IX

S. A. E. 1117, carburized at 1750° F. in an atmosphere prepared from an air-gas ratio of 200-75 cc/minute through hot charcoal and cooled slowly in the retort. (Etched with 2 percent nital.) X75.

	Time in hours	Case depth in inches
Figure 16	5	0.082
Figure 17	4	0.060
Figure 18	3	0.043
Figure 19	2	0.032
Figure 20	1	0.020

PLATE IX

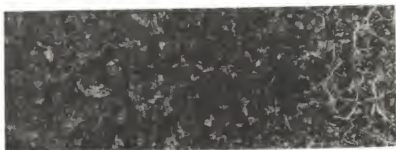


Figure 16

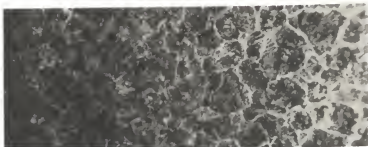


Figure 17

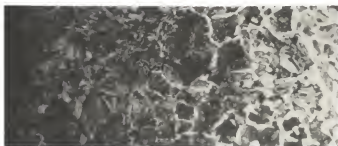


Figure 18

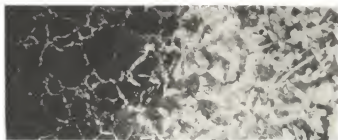


Figure 19

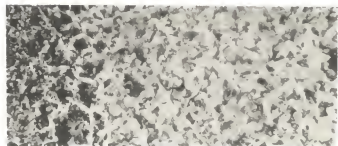


Figure 20

EXPLANATION OF PLATE X

S. A. E. 1117, carburized at 1600° F. in an atmosphere prepared from an air-gas ratio of 300-275 cc/minute through hot charcoal and cooled slowly in the retort. (Etched with 2 percent nital.) X75.

	Time in hours	Case depth in inches
Figure 21	5	0.039
Figure 22	4	0.030
Figure 23	3	0.027
Figure 24	2	0.022
Figure 25	1	0.014

PLATE X

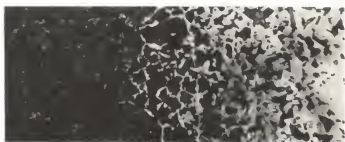


Figure 21



Figure 22



Figure 23



Figure 24

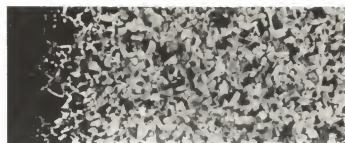


Figure 25

EXPLANATION OF PLATE XI

S. A. E. 1117, carburized at 1675° F. in an atmosphere prepared from an air-gas ratio of 300-275 cc/minute through hot charcoal and cooled slowly in the retort. (Etched with 2 percent nital.) X75.

	Time in hours	Case depth in inches
Figure 26	5	0.046
Figure 27	4	0.040
Figure 28	3	0.037
Figure 29	2	0.027
Figure 30	1	0.022

PLATE XI



Figure 26

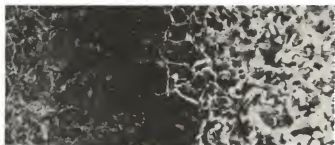


Figure 27

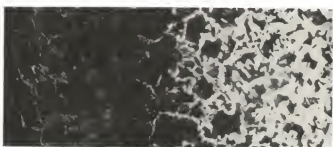


Figure 28

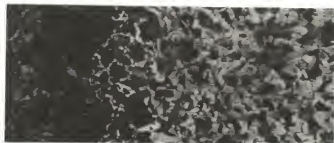


Figure 29



Figure 30

EXPLANATION OF PLATE XII

S. A. E. 1117, carburized at 1750° F. in an atmosphere prepared from an air-gas ratio of 300-275 cc/minute through hot charcoal and cooled slowly in the retort. (Etched with 2 percent nital.) X75.

	Time in hours	Case depth in inches
Figure 31	5	0.072
Figure 32	4	0.062
Figure 33	3	0.046
Figure 34	2	0.040
Figure 35	1	0.027

PLATE XII

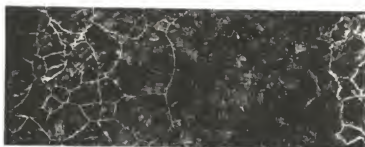


Figure 31



Figure 32

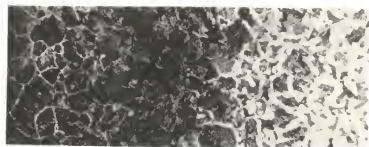


Figure 33

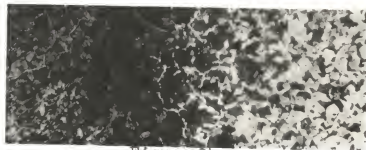


Figure 34

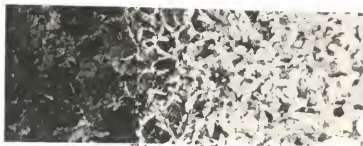


Figure 35

SUMMARY AND CONCLUSIONS

1. When a slow flow of the carburizing gas was used irregular case depths were likely to result.
2. If the rate of flow was too great the soot which formed was hard and somewhat difficult to remove.
3. Natural gas is a very strong carburizing agent and will supply more carbon than is necessary.
4. By the proper proportioning and regulation, natural gas and air flowing through hot charcoal will give cases of desired depth and characteristics.
5. By the proper proportioning and regulation, natural gas and air flowing through hot charcoal will be neutral to the steel being heat treated.
6. The rate of diffusion, in general, is dependent upon the carbon potential of the carburizing atmosphere.
7. There is a retarding of the rate of carburization when soot has been deposited on the specimen and especially when the soot is hard and impervious.
8. With a substantial decrease in the charcoal supply, the gas analysis changed in composition. There was not as complete reduction of the oxidizing components resulting in a less active carburizing atmosphere.
9. At the lower temperature (1600° F.) the dew point had a tendency to be higher.
10. A fan within the retort was necessary to give adequate circulation for the production of uniform case depths.

ACKNOWLEDGMENT

The author wishes to express his gratitude to Dr. A. E. Hostetter, major instructor, for his guidance throughout the experimental work and the preparation of this thesis; to Prof. G. A. Sellers, Head of the Department of Shop Practice, and Prof. D. E. Zabel for their cooperation and assistance in making this investigation possible.

LITERATURE CITED

- (1) Becker, M. L.
Carburizing and graphitizing reactions between iron-carbon alloys and CO and CO₂. Iron and Steel Inst. Jour. 121: 337-361. 1930.
- (2) Bramley and Associates.
Carnegie Scholarship Memoirs. 27-29. 1926.
- (3) Burrell Gas Analysis and Apparatus Catalog 80.
Pittsburgh: Burrell Technical Supply Co. 1950.
- (4) Carburizing.
Symposium. Amer. Soc. for Metals. 1942.
- (5) Controlled Atmospheres.
Symposium. Amer. Soc. for Metals. 1942.
- (6) Cowan, R. F.
Metal progress. Amer. Soc. for Metals. 24: 44. October, 1933.
- (7) Fisher, A. J.
Furnace atmospheres. Baltimore: C. M. Kemp Mfg. Co. 1937.
- (8) Frischman, F. A.
Good carburizing practice. Amer. Mach. 94 (24). March 5, 1951.
- (9) Gillett, H. W.
Metals and alloys. 6: 324. November, 1935.
- (10) Gillett, H. W.
Controlled atmospheres in steel treating. Metals and Alloys. 6: 195. August, 1935.
- (11) Giolitti, F.
Cementation of iron and steel. New York, 1915. Original not seen. Carburizing Symposium. Amer. Soc. for Metals. 1938.
- (12) Grossman, M. A.
Carburizing symposium. Amer. Soc. for Metals. 1938.
- (13) Groves, W. T.
Dew point vs percent CO₂ as furnace atmosphere control check. Industrial Heating. 16: 966. June, 1944.

- (14) Guthrie, R. G. and R. Wozasek.
Amer. Soc. for Steel Treating Trans. 19: 853. 1927.
- (15) Harris, F. E.
Carburizing and diffusion data. Metal Progress. Amer.
Soc. for Metals. 6d: 265. August, 1943.
- (16) Harris, F. E.
Atmosphere applications, equipment, methods and process
cycles. Metal Progress. Amer. Soc. for Metals. 47: 713.
April, 1945.
- (17) Harris, R. P. and W. H. Holcroft.
Nitrogen as a carrier gas in gas carburizing. Metal
Progress. 53: 241. February, 1948.
- (18) Heyer, R. H.
Engineering physical metallurgy. New York: D. Van Nos-
trand, 549 p. 1948.
- (19) Holcroft, W. H. and E. C. Bayer.
Continuous gas carburizing without gas generator. Materi-
als and Methods. 26: 92-93. October, 1947.
- (20) Holcroft Co.
Controlled atmosphere heat treating furnaces. Detroit:
Holcroft Co. 1939.
- (21) Holcroft W. H. and R. P. Harris.
Nitrogen as a carrier gas. Metal Progress. 53: 241.
February, 1949.
- (22) Holcroft, W. H. and M. P. Larson.
Generators for controlled atmospheres. Steel. January,
1949.
- (23) Jominy, W. E.
University of Michigan Engineering Research Bulletin 18.
Ann Arbor, Michigan. 1931.
- (24) Malcolm, V. T.
Carburizing symposium. Amer. Soc. for Metals. 1938.
- (25) McQuaid, H. W.
Gas carburizing. Surface Combustion Corp., Toledo, Ohio.
n. d.
- (26) McQuaid, H. W.
Metal Progress. 26: 22. 1934.
- (27) Metals Handbook.
American Society for Metals. 1444 p. 1948.

- (28) Rengstorff, G. W. P., M. B. Meyer, and C. L. Floe.
The carbonitriding process of case hardening steel. Amer.
Soc. for Metals Trans. 1950.
- (29) Rowland, B. S. and S. R. Lyle.
The application of M_s points to case depth measurements.
Amer. Soc. for Metals Trans. 37: 27. 1946.
- (30) Sisco, F. T.
Modern metallurgy for engineers. New York: Pitman,
499 p. 1948.
- (31) Smith, J. B.
Safety procedures. Industrial Heating. 17: 592. April,
1950.
- (32) Stansel, N. R.
Industrial electric heating. New York: John Wiley and
Sons, 444 p. 1933.
- (33) Sykes, W. P.
Carburizing iron by mixtures of hydrogen and methane.
Amer. Soc. for Steel Treating Trans. 12: 737. 1927.
- (34) Widrig, S. L., J. E. Reed, and O. E. Cullen.
Suspended carburization. Materials and Methods. 25: 65.
February, 1947.
- (35) Wilbur and Comstock.
Amer. Soc. for Steel Treating Trans. Vol. 18. 1930.
- (36) Williams, G. T.
Gaseous media for carburizing. Carburizing symposium.
Amer. Soc. for Metals. 1938.
- (37) Wyzalek, J. F. and M. H. Folkner.
Metal Progress. 38: 261. Amer. Soc. for Metals. Septem-
ber, 1940.

CERTAIN PROCEDURES IN UTILIZING KANSAS
NATURAL GAS AS A CARBURIZING AGENT

by

FRANK JACOBS, JR.

B. S. Kansas State College of
Agriculture and Applied Science, 1950

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the
requirements for the degree

MASTER OF SCIENCE

Department of Shop Practice

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE
1951

An experimental gas carburizing apparatus was designed, constructed, and utilized under various conditions. The main feature of the apparatus was the tube containing charcoal through which the gases flowed at the carburizing temperature. This preparation of the carburizing atmosphere took place within the retort, thus eliminating the need for an outside generator. One standard test specimen of low carbon steel (S. A. E. 1117) was carburized under various conditions. Carburizing was done at temperatures of 1600, 1675, and 1750° F. in an atmosphere which varied according to the percentage of air added to the natural gas. Carburizing in 100 percent natural gas was also investigated. The carburizing period varied from one to five hours. At the end of the carburizing period, the gas was shut off and the retort was closed to the outside atmosphere and the specimen was allowed to cool slowly in the retort. The effects of these variables were evaluated on the basis of total depth of penetration, rate of flow of the carburizing gas, composition of the carburizing atmosphere, amount of soot deposited in the retort, and the mechanical arrangement for the flow of gases through the retort.